

LOW TEMPERATURE ELECTRON PARAMAGNETIC STUDIES IN VANADIUM PHOSPHATE GLASSES

By

L. I. HORVÁTH

Institute of Biophysics, Biological Research Center, Szeged

and

T. SZÖRÉNYI

Institute of Experimental Physics, Attila József University,
Szeged

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In vanadium phosphate glasses the paramagnetism is due to the conducting 3d electrons of V^{4+} centers and, thus, the electron exchange frequency between V^{4+} and V^{5+} ions as followed by EPR lineshape analysis can furnish direct information on the mobility of the charge carrier. In the central region of the spectrum where the parallel and perpendicular lines overlap the characteristic hopping frequency can be followed through two orders of magnitude. If spin-spin interaction should also be taken into account, the temperature dependence of paramagnetic susceptibility provides useful structural data.

Introduction

The diverse application of semiconducting glasses results in a need for deeper understanding of the physical events in these materials; a challenge which has initiated both thorough theoretical and experimental work. In vanadium phosphate ($V_2O_5-P_2O_6$) glasses the conduction mechanism can be described in terms of phonon assisted hopping of electrons between V^{4+} and V^{5+} ions [1, 2]. Since electron paramagnetic resonance (EPR) provides information about the 3d electron of the V^{4+} ion, it has been widely used to study the short range order around the V^{4+} centers. However, the lineshape analysis of the EPR spectra which can furnish information about the dynamical behaviour of the conducting 3d electrons gained less interest. LIVAGE *et al.* found that in amorphous vanadium pentoxide the paramagnetic resonance exhibited hyperfine splitting (hfs), whereas in crystallized samples no hyperfine splitting could be resolved. They interpreted this phenomenon by considering the electron delocalization to an adjacent vanadium nucleus, and gave an upper limit for the hopping frequency [3, 4]. A complete EPR analysis can, thus, reveal not only structural aspects but also dynamical features. From EPR theoretical point of view V^{4+} is one of the most extensively studied transition metal ions and its application is not limited to vanadium containing systems as it is indicated by the current interest of introducing V^{4+} spin probes into different materials.

Since we are interested in the anomalous conductivity properties of vanadium phosphate glasses which may be of both microstructural and dynamical origin [5, 6], in a series of investigations we analysed the EPR lineshape of these glasses. It turned out that for glasses with low V^{4+} content the lineshape analysis could be quantitatively done, but beyond a certain V^{4+} content the hfs analysis broke down due to the concomitant line broadening of spin-spin interaction. LIVAGE and his coworkers observed no exchange narrowing down to liquid nitrogen temperature [3, 4]. On theoretical basis, however, exchange narrowing might be anticipated at low temperatures, and thus we extended the temperature range down to 20 K.

Experimental

EPR measurements were made with a JES-PE-IX (Jeol, Japan) X-band spectrometer using 100 kHz standard or 100 kHz/80 Hz double modulation techniques. For cryogenic work we applied a closed-cycle He cryostat (DISPLEX™, Air Products, USA; model CSW-202), which very economically extended our temperature range down to 20 K. This system permits flexibility by having a small expander conveniently mounted above the EPR cavity while compressor and controls are remotely located. The expander module consists of a two-stage piston: the first stage maintains the "warm" end of the second stage at low temperature (90 K). The samples are attached to the cold end of the second stage. The rate of cool down depends on the mass which is attached to the cold end and also the conductance of the heat path between the sample and the cold end. The system is thermally insulated from ambient conditions with a vacuum shroud. A vacuum of 5×10^{-4} torr or better is required to achieve good performance, which was done by connecting the expander module to a PST-60 E vacuum pumpstand (Balzers, Liechtenstein). The inevitable mechanical vibration of the sample due to the moving piston was minimized by mounting the expander module onto a bulky ϕ - z translator.

The temperature was measured with a Chromel *vs.* gold — 0.07 at. % iron thermocouple at the cold end of the second stage. The heat path was manufactured from a single piece copper rod in order to minimize wrong heat conductance due to copper-to-copper soldering. The temperature was varied with a kanthal heating coil attached to the cold end of the second stage. As the kanthal coil warms up the cold end it reduces the cooling rate and, thus, the sample — through the heat path — equilibrates very fast with the cold end. The time period to establish any heat equilibria was monitored by the EPR signal intensity and a typical value of about 10 minutes was found (in 10 K steps).

During EPR measurements both the vacuum shroud and the cooled sample should be inserted into the cavity. Since the Q factor (which is proportional to the sensitivity) largely depends on the dielectric constant of the sample, only moderate amount of metal can be applied inside the cavity. This requirement was met by using a 1 mm dia. copper wire at the end of the heat path and a 11 mm O.D. quartz vacuum shroud (Fig. 1a).

The vanadium phosphate glasses were prepared from V_2O_5 and H_3PO_4 (Reanal, Hungary, purum grade). The V^{4+}/V_{total} ($=c$) ratio was varied by melting the mixtures at various temperatures. As shown in Fig. 1a the samples were made by

immersing the end of the copper wire into the melt. The obtained material proved to be totally amorphous by X-ray diffraction and scanning electron microscopy.

Thermostatic analysis of the experimental set-up

From thermostatic point of view the set-up can be represented by the flow diagram given in Fig. 1b. Three factors determine the actual temperature of the sample: firstly the rate of the heat transmission between the cold end (heat sink) and the sample (denoted by 4→3→1 in Fig. 1b), secondly the rate of the radiation heat of the ambient heat reservoir which warms up the sample (5→4), and thirdly the heating rate of the coil which reduces the heat sinking efficiency of the cold end (2→1). Obviously an EPR application of the system is the most critical test, since in this case the sample is relatively far from the cold end and no silvered quartz extension tube can be applied to minimize the radiation heat. Less apparently, this transparent tube has other disadvantages too, for its geometrical sizes make very troublesome to provide a really efficient vacuum isolation. Needless to say whenever there was a heat conductance coupling between the ambient heat reservoir and the sample (Fig. 1b, dotted line 5→4), with its moderate heat sinking capacity (2 Watts) the cold end could hardly lower the temperature of the sample below room temperature. A typical case repeatedly experienced occurred when the sample touched the inner surface of the extension tube. However, with careful alignment of the sample this error could be prevented.

Another weak point of this system is to obtain maximum heat coupling between the sample and the cold end. As far as vanadium phosphate glass is concerned this is an almost ideal substance since the melted glass wets the copper wire. Still, the good heat contact becomes worse at low temperatures due to differences between the linear expansion's coefficient of the copper wire and the glassy substance. In some cases the glass chipped off when exposed to cooling. This problem could be best overcome by applying a special cryogenic heat conducting grease (CRY—CON, Air Products, USA) which provided good heat contact on the outer surface of the glass-metal joint.

Results and discussion

LIVAGE and his coworkers found that the EPR lineshape of amorphous V_2O_5 and V_2O_5 — P_2O_5 glasses with more than 92 mol % V_2O_5 strongly depended on temperature: the hfs linewidth changed by one order of magnitude between 273 K and 77 K [4, 7]. To interpret the results they considered the electron delocalization.

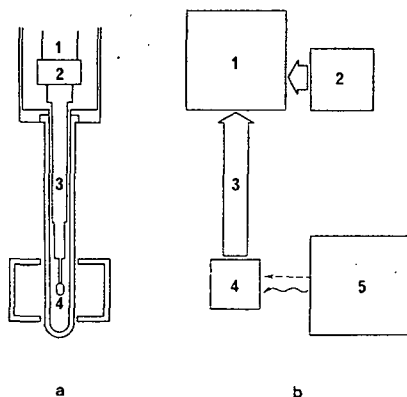


Fig. 1. The lay-out of mounting the glassy sample onto the cold end of the He-cryostat (a) and its thermostatic flow diagram (b). (1) — cold end, (2) — heating coil, (3) — heat transferring copper rod, (4) — glassy sample inside the EPR cavity, (5) — ambient heat reservoir (including the cavity).

to an adjacent vanadium nucleus, cf. the motion of the magnetic electron towards the nearest hopping center. Since the hopping motion is a thermally activated process, at higher temperatures more complete electron delocalization and, thus, worse hfs resolution can be anticipated.

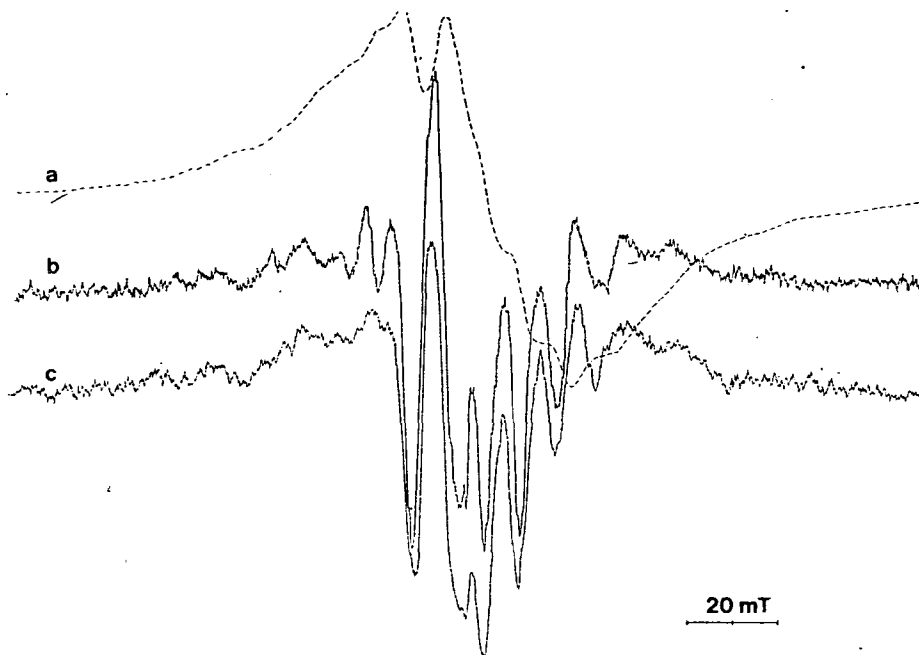


Fig. 2. Temperature dependence of the hyperfine structure in a 90–10 glass, $c=0.05$. Curve a (dotted line) first derivative spectrum, curves b and c second derivative spectra recorded at 20 and 300 K, respectively.

In Fig. 2 the temperature dependence of the EPR spectrum is shown for a 90 mol % V_2O_5 –10 mol % P_2O_5 (90–10) glass. Since the hfs could be resolved only partially at room temperature, second derivative representation was chosen which is very sensitive to changes in the overall lineshape. As seen in Fig. 2 (curves b and c) the hfs resolution could slightly be improved when the sample was cooled down to 20 K. To make a quantitative estimation in this respect we assume that two overlapping spectral lines can only be resolved if their midpoint is not closer to each other than their spectral linewidth. According to LIVAGE ET AL. when this condition is met, the hopping frequency cannot be higher than the linewidth expressed in frequency units. However, it should be noted that this analysis holds in this simple form for a spectral doublet only. The V^{4+} axial spectrum represents a much more complicated case where a full lineshape analysis is not straightforward.

The EPR spectrum of the same glass dissolved in 38 wt % sulphuric acid is shown in Fig. 3. This exhibits characteristic hyperfine splitting due to the ^{51}V

nucleus $\left(I = \frac{7}{2}\right)$ which is in an axially distorted crystal field. The spin-Hamiltonian can be written in the following form:

$$\hat{H} = \beta g_{\parallel} B_z S_z + \beta g_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where g_{\parallel} , g_{\perp} and A_{\parallel} , A_{\perp} denote the axial components of the \hat{g} - and \hat{A} -tensor, respectively; S_x , S_y , S_z and I_x , I_y , I_z are the three components of the electron and nuclear spin operators, B_x , B_y , B_z denote the magnetic field strength along the principal axes, and β is the Bohr magneton [4, 7]. In good agreement with the literature data we found $g_{\parallel} = 1.936$, $g_{\perp} = 1.987$, $A_{\parallel} = 20.1$ mT, and $A_{\perp} = 6.7$ mT.

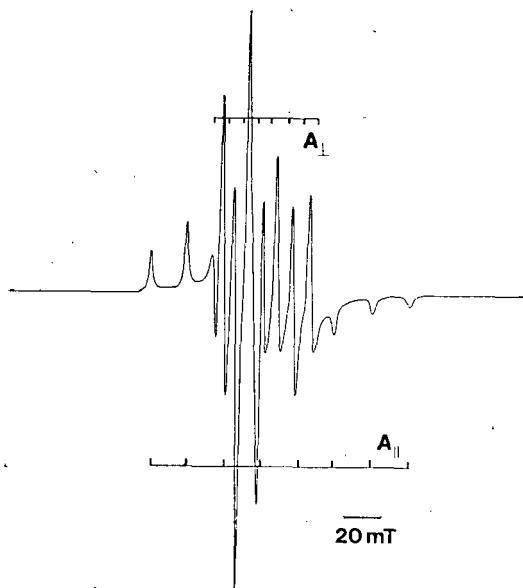


Fig. 3. The EPR spectrum of a frozen solution of V^{4+} recorded at 77 K.

As schematically shown in Fig. 3 the \hat{A} -tensor exhibits large anisotropy resulting in many overlapping lines. Using second order perturbation formulae we calculated the position of each parallel and perpendicular line and determined the positional differences in frequency units (Table I). It is very interesting to realize that in the central region where the parallel and perpendicular features overlap a few lines are much closer than those in the wings. As a necessary consequence an ideally resolved hfs spectrum should first collapse in this region indicating slow hopping rate. It is straightforward to extend the analysis of the wings [7] to the whole spectrum since with a careful analysis of the hfs particularly in the central region the increase of the hopping frequency can be followed quantitatively through almost two orders of magnitude. To illustrate the method we analyzed the spectra

Table I

The position and differences of the parallel and perpendicular features in the axial spectrum of V^{4+} ions

Position in mT units	Assignment	Difference	
		in mT	in MHz
417.63	$\parallel \left(-\frac{7}{2} \right)$		
397.14	$\parallel \left(-\frac{5}{2} \right)$	20.49	567.
376.78	$\parallel \left(-\frac{3}{2} \right)$	20.36	564.
360.89	$\perp \left(-\frac{7}{2} \right)$	15.89	440.
356.54	$\parallel \left(-\frac{1}{2} \right)$	4.35	120.
352.21	$\perp \left(-\frac{5}{2} \right)$	4.33	120.
344.19	$\perp \left(-\frac{3}{2} \right)$	8.02	222.
337.22	$\parallel \left(+\frac{1}{2} \right)$	6.97	193.
336.82	$\perp \left(-\frac{1}{2} \right)$	0.4	11.
330.12	$\perp \left(+\frac{1}{2} \right)$	6.7	185.
324.09	$\perp \left(+\frac{3}{2} \right)$	6.03	167.
318.71	$\perp \left(+\frac{5}{2} \right)$	5.38	149.
316.73	$\parallel \left(+\frac{3}{2} \right)$	1.98	55.
312.83	$\perp \left(+\frac{7}{2} \right)$	3.9	108.
296.37	$\parallel \left(+\frac{5}{2} \right)$	16.46	456.
276.14	$\parallel \left(+\frac{7}{2} \right)$	20.23	560.

shown in Fig. 2. In the left side of the spectra two lines (assigned to $m = +\frac{7}{2}$ perpendicular and $m = +\frac{3}{2}$ parallel transitions) are clearly resolved at 20 K (curve b) whereas at 300 K (curve c) this pattern can hardly be recognized. According to Table I we can conclude that the exchange frequency is about 100 MHz at 300 K. Analyzed in very much the same way for other linepairs we can establish

that this frequency value drops to its half at 20 K. From these values the activation energy of the hopping process can be estimated [8]: $E_h = 1.2$ meV.

We investigated a series of 90–10 and 75–25 glasses with varying c -values. At higher V^{4+} content no hfs could be resolved at all even at 20 K (Fig. 4a–d). Therefore we concluded that apart from lifetime broadening dipole broadening should also contribute to the linewidth. In fact in the case of glasses with low c -values we are already in the region where the contribution of lifetime and dipole broadening to the resultant linewidth is comparable in size, whereas at higher c -values the linewidth is entirely governed by dipolar broadening. This is a reasonable explanation whenever $V^{4+} - V^{4+}$ interaction cannot be neglected. [5].

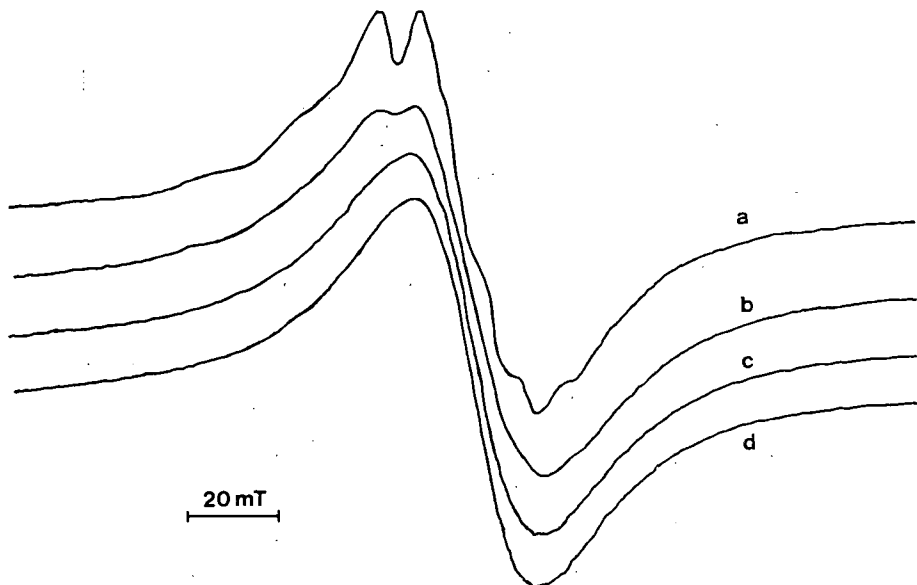


Fig. 4. EPR spectra of V_2O_5 – P_2O_5 glasses: (a) 90–10, $c=0.07$; (b) 75–25, $c=0.10$; (c) 90–10, $c=0.14$; (d) 75–25, $c=0.28$

In this case an additional term should be included into the spin-Hamiltonian (\hat{H}) given in Eq. (1). Assuming pairwise spin-spin interaction between the nearest neighbours 1 and 2 we can write:

$$\hat{H}' = \hat{H} + J(c) \bar{S}_1 \bar{S}_2 \quad (2)$$

where \bar{S} denotes the spin operator, $J(c)$ is the triplet-singlet separation energy (in eV) which depends on the average distance of the V^{4+} centers. (No anisotropic exchange was observed.) $J(c)$ can be obtained from the temperature dependence of EPR signal intensities (*cf.* paramagnetic susceptibility). As seen in Fig. 5 the paramagnetism of this 75–25 glass does not follow Curie-law (*i.e.* reciprocal temperature dependence), but exhibits slight spin exchange.

It turned out quite apparently that the lineshape analysis may be applied only to few exceptional glasses (with very low c -values) but no data can be obtained for the majority of the vanadium phosphate glasses since the dipolar broadening do-

minates the resultant linewidth. In glasses rich in V^{4+} the $J(c)$ value can be introduced which is related to the average spacing of the hopping centers. This is a geometric factor and is, thus, a static parameter; still it should be noted that the hopping frequency — apart from the degree of level matching and the barrier height — also depends on the hopping distance. Therefore, the $J(c)$ value furnishes useful information on the structure of the glass. A systematic investigation of $J(c)$ in the same $V_2O_5-P_2O_5$ glass series will be reported in a forthcoming publication.

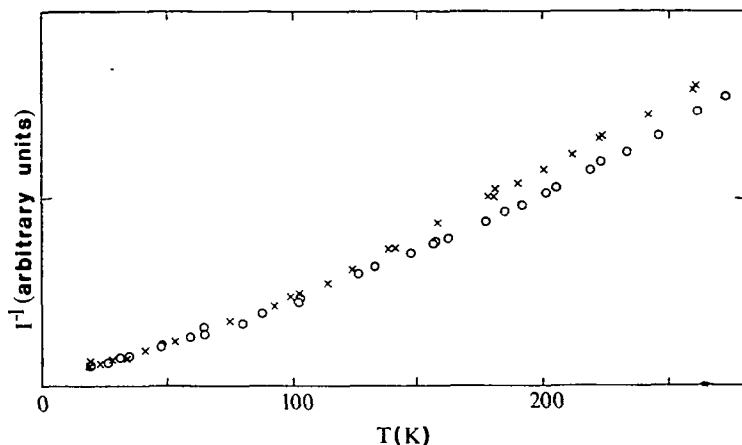


Fig. 5. Temperature dependence of the EPR signal intensities in a 75–25 glass, $c=0.26$. The two sets of experimental points illustrate the reproducibility of this measurement from one sample to another.

Summing up we can conclude that EPR can also provide a means to derive dynamical parameters, not necessarily limited to the $V_2O_5-P_2O_5$ system. For glasses with very low V^{4+} content the lineshape analysis can be applied; the limit and, thus, the applicability of which depends on the hyperfine coupling constant of the transition-metal ion studied. Beyond this limit the hfs analysis breaks down due to the spin-spin interaction; an effect which provides an alternative way to analyze the hopping conditions.

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ИЗУЧЕНИЕ СТЕКОЛ ФОСФАТА ВАНАДИЯ МЕТОДОМ ЭПР ПРИ НИЗКИХ ТЕМПЕРАТУРАХ

Л. И. Хорват и Т. Сереньи

Частота электронного обмена между V^{4+} и V^{5+} ионами, определенная из анализа форм ЭПР линий, дает непосредственную информацию о подвижности носителей заряда.